

PTO/SB/05 (12/97)

Approved for use through 09/30/00. OMB 0651-0032

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

**UTILITY
PATENT APPLICATION
TRANSMITTAL**

(Only for new nonprovisional applications under 37 CFR 1.53(b))

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. Fee Submission Form
(Submit an original, and a duplicate for fee processing)
2. Specification [Total Pages 22] (preferred arrangement set forth below)
 - Descriptive title of the Invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to Microfiche Appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
3. Drawing(s) (35 USC 113) [Total Sheets]
4. Oath or Declaration [Total Pages]
 - a. Newly executed (original or copy)
 - b. Copy from a prior application (37 CFR 1.63(d)) (for continuation/divisional with Box 17 completed)
(Note Box 5 below)
 1. DELETION OF INVENTOR(S)
Signed statement attached deleting Inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
5. Incorporation By Reference (useable if Box 4b is checked)
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference thereto.

Attorney Docket No.	99A209	Total Pages	25
First Named Inventor or Application Identifier			
Qing Min WANG			
Express Mail Label No.	EE295479125US		

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

6. Microfiche Computer Program (Appendix)
7. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
 - a. Computer Readable Copy
 - b. Paper Copy (identical to computer copy)
 - c. Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

8. Assignment Papers (cover sheet & document(s))
9. 37 CFR 3.73(b) Statement (when there is an assignee) Power of Attorney
10. English Translation Document (if applicable)
11. Information Disclosure Statement (IDS)/PTO-1449 Copies of IDS Citations
12. Preliminary Amendment
13. Return Receipt Postcard (MPEP 503) (Should be specifically itemized)
14. Small Entity Statement filed in prior application, Statement(s) Status still proper and desired
15. Certified Copy of Priority Document(s) (if foreign priority is claimed)
16. Other: _____

17. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

Continuation Divisional Continuation-in-part (CIP) of prior application No: _____

18. CORRESPONDENCE ADDRESS

Customer Number or Bar Code Label  or Correspondence address below
(Ins) 020411 (label here)

NAME	Philip H. Von Neida		Reg. No. 34,942
	Patent, Trademark and Licensing Department		
ADDRESS	The BOC Group, Inc.		
	100 Mountain Avenue		
CITY	Murray Hill	STATE	NJ
COUNTRY	USA	TELEPHONE	908-771-6402
		ZIP CODE	07974
		FAX	908-771-6159

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231.

00/15/90
+
05/31/00

EXPRESS MAIL MAILING LABEL: EE295479125US

IMPROVED ACID COPPER ELECTROPLATING SOLUTIONS

This application claims priority from Provisional Patent Application Number
5 60/144,159 filed July 15, 1999.

FIELD OF THE INVENTION

The present invention is related to an improved acid copper electroplating
10 composition. More particularly, the present invention relates to the use of new
carriers, brighteners and levelers as well as molecules that combine carrier/brightener
and carrier/leveler functionality.

BACKGROUND OF THE INVENTION

15 Copper electroplating bath solutions are used in a variety of industries. In the
semiconductor industry, there is an increasing need for these baths to meet decreasing
device feature size, increasing wafer size and high yield. Various proprietary
electroplating bath chemistries are commercially available that claim success with
20 regards to the copper metallization process. Ideally, the bath chemistry should help to
fill with copper small yet high aspect ratio trenches and vias, e.g. < 0.18 μ m and
aspect ratio > 5, to obtain uniform and void free plating while maintaining high
production rates. The plating bath chemistries should also be relatively chemically
stable, less corrosive and easily monitored and replenished.

25 Copper sulfate and sulfuric acid are the basics of the acid copper electroplating
bath chemistry. Organic additives such as carriers, brighteners, levelers and
combinations of these can offer a plating bath to fill the small and high aspect ratio

trenches and vias without voids or seams. As-plated copper deposits are of uniform thickness and fine grain size, and highly <111> crystal orientated.

Carriers typically are water-soluble polymers containing $-(\text{CH}_2)_n-\text{O}-$ where $n =$

5 1 to 3 or branched derivatives in the main chains. Carriers can form a monolayer film at the cathode surface, which is a barrier to the diffusion of Cu^{+2} ions to the surface and polarizes the cathode. The proper polarization of the cathode is a prerequisite for producing fine and orientated grain structure. However, carriers tend to decompose into lower molecular fragments at both the cathode and the anode, and lose

10 polarization effectiveness. As such, carriers with high stability are desired.

Brighteners not only produce fine and orientated grain structure for the as-plated deposits but also provide better chemical stability and solubility in the electroplating bath. Brighteners are typically water-soluble sulfonic acids containing

15 mercapto and/or thio groups. U. S. Pat. No. 5,151,170 teaches a brightener that consists essentially of the hydrogen peroxide oxidation product of a dialkylamino-thioxomethyl-thioalkanesulfonic acid wherein each alkyl and alkane group individually contains 1 to 6 carbon atoms. They can produce fine copper deposits by masking the preferential growth sites/planes. Current brighteners can suffer from

20 poor stability, oxidation by air and electrochemical oxidation at the anode, as well as catalytic decomposition at the copper surface. The decomposed products are often detrimental to copper deposition properties.

Levelers play a key role in void and seam free trench filling, *i.e.*, superfilling or bottom-up filling. The deposition rate needs to be much faster at the bottom of the features than on the side wall and shoulder of the trenches and vias. As such, different molecular size levelers are employed to tailor different generation (or size) of trenches and vias. The large molecular size is usually preferred for the filling of larger trenches and vias since the diffusion of the levelers towards the bottom of trenches is

25 much slower, which in turn, results in extremely low leveler flux at the bottom and promotes bottom-up filling or superfilling. However, the larger molecular size can eventually block the openings and prevent the copper ions from entering the trenches.

This consequently creates voids when the size of the trench and vias is greatly reduced (e.g., ~0.1 μ m).

Various chemically combined brightener/carrier and/or leveler/carrier can
5 further enhance these functions and goals. The as-plated copper deposits can
complete self-annealing process in several hours to have a stable microstructure at
room temperature.

DESCRIPTION OF THE RELATED ART

10

U.S. Pat. No. 5,051,154 teaches an aqueous electroplating solution comprising at least one soluble copper salt, an electrolyte and at least one organic additive capable of modifying the charge transfer overpotential of the solution in an amount sufficient to shift the overpotential by at least 150 millivolts and being independent of solution
15 agitation. This reference teaches using a wetting agent as a component additive in the system capable of modifying the charge transfer overpotential. Additional additives can include a brightener along with the wetting agent and this can be selected from the group consisting of *n,n*-dimethyl-dithiocarbamic acid - (3-sulfopropyl) ester; 3-mercaptopropylsulfonic acid(sodium salt); carbonic acid-dithio-*o*-ethylester-*s*-ester
20 with 3-mercaptop-1-propane sulfonic acid(potassium salt); bisulfopropyl disulfide; 3-(benzthiazolyl-*s*-thio) propyl sulfonic acid (sodium salt); and pyridinium propyl sulfobetaine. The three component additive may also include levelers such as those selected from the group including 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine; 2-mercaptopthiazoline; ethylene thiourea; thiourea; and alkylated
25 polyalkyleneimine.

DETAILED DESCRIPTION OF THE INVENTION

30 The present invention provides for an improved acid copper electroplating bath composition and method for preparing them. The composition comprises an aqueous solution of acid and copper salt, and the improvement comprises the addition of at least one of a carrier; a water soluble mercapto-containing organic brightener

compound; and a leveler which comprises an organic compound containing single or multiply charged centers in acidic bath solution.

In addition the present invention provides for a method for copper plating or
5 metallization of advanced interconnects (less than 0.18 microns and having an AR
(Aspect Ratio) greater than 6) comprising immersing a substrate intended for
advanced interconnects into the copper electroplating composition and conducting an
electrochemical deposition process.

10 In a typical acid copper electroplating bath, an acid and copper salt are
employed. The acid is typically sulfuric acid while the copper salt can be selected
from the group consisting of copper sulfate, copper acetate, copper fluoborate, cupric
nitrate and copper pyrophosphate. Additional inorganic additives can include both
chloride and alkaline species. The chloride can enhance cathode surface adsorption of
15 organic additives such as the carrier and improve the oxidation of the anodes to
improve plating efficiency. Alkaline species such as ammonium hydroxide are added
to reduce the acidity and corrosivity of this bath solution. Chloride is added in an
amount of about 20 to 100 parts per million parts water in the bath, while the alkaline
is added in an amount necessary to reduce the solution's pH.

20 For the purposes of the present invention, the acid copper electroplating
solution will have from about 50 to about 250 grams of copper salt per liter of water
and about 60 to about 250 grams of sulfuric acid per liter of water.

25 In addition to sulfuric acid, copper salt, and inorganic additives disclosed
above, as is known in the art, one or more of organic additives such as carriers,
brighteners, levelers, and combinations of these are also employed to obtain high
throwing power to fill the small and high aspect ratio trenches and vias.

30 The carriers used in this invention can comprise conventional ones in the art,
e.g., polyethylene glycol and poly(ethylene oxide), and a new class of carriers -
polysaccharides. The polysaccharides consist of simple sugars such as fructose and

DRAFT - 08/20/2009

glucose linked by glycosidic bonds. Representative examples include but are not limited to starch, cellulose, amylopectin and amylose.

The brighteners useful in this invention possess both stability and solubility in the copper electroplating bath. The brighteners include both water soluble mercapto-containing organic compounds and other organic sulfides. Representative examples include but are not limited to *N*-methylallyl-*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 3-mercaptopropanesulfonic acid sodium salt; 3-mercaptopropanesulfonic acid; bis (2-mercaptoproethyl) sulfide; ethylene trithio carbonate; ethanethiol; 2-mercaptopropanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thioglycolic acid. The most preferred brighteners are ammonium diethyldithiocarbamate, 3-mercaptopropanesulfonic acid sodium salt, and its free acid form. 3-Mercaptopropanesulfonic acid is prepared from 3-mercaptopropanesulfonic acid sodium salt by an ion-exchange process using cation ion-exchange resins such as Dowex DR2030 (20-30 mesh), Dowex HCR-W2 (16-40 mesh), Dowex 50Wx8-100 (50-100 mesh, 1.7 meq / mL, 0.80 g / mL), and Dowex 50Wx8-200 (100-200 mesh, 1.7 meq / mL, 0.80 g / mL). The sodium level can be reduced to a few ppm from ~1500 ppm in original 1 wt.% aqueous solution. Both a packed column with ion-exchange resin and a reaction flask approach using ion-exchange resin can remove sodium to low ppm levels.

The need for a sodium-free brightener is important in avoiding sodium contamination of the copper deposited thin layer. The 3-mercaptopropanesulfonic acid was prepared by both ion-exchange column and in a reaction flask, and sodium removal efficiency was better than 99% for both methods. This is important regarding bath life as the buildup of sodium in the bath over time would require the bath to be dumped and replenished once the sodium level becomes unacceptably high.

The levelers useful in this invention possess single or multiple positively charged centers that will form single or multiple positively charged sites after protonation in the acidic conditions of the bath. In this invention, the levelers are divided into three groups - polymeric levelers, low molecular weight

levelers, and organic dyes. Representative examples of polymeric levelers include but are not limited to polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly(bis(2-chloroethyl)ether, *cis*-1,2-bis[2-

(dimethylamino)propyl]urea, quaternized; poly[*N,N'*-bis(2,2,6,6-tetramethyl-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine]; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline). The most preferred polymeric leveling agents are poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(diallyldimethylammonium chloride).

Representative examples of low molecular weight leveling agents include but are not limited to:

15 limited to *N*-containing acyclic systems, *N*-containing five-membered heterocyclic systems, and *N*-containing six-membered heterocyclic systems. Most of them also contains mercapto-, sulfide, or disulfide functionalities. Representative examples of *N*-containing acyclic systems include 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, and diethylenetriamine. The most preferred one is diethylenetriamine.

20 Representative examples of *N*-containing five/six-membered heterocyclic systems include *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride,

25 5-phenyl-1 *H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1 *H*-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4 *H*-1,2,4-triazole-3-thiol, diethyl heptadecenyl imidazolinium ethylsulfate, hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopurine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopurine, 4,5-diamino-6-hydroxy-2-mercaptopurine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercaptop-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinolinethiol, 5-carbethoxy-2-thiouracil, 1 *H*-1,2,4-triazole-3-thiol, 1-phenyl-1 *H*-1,2,4-triazole-5-

30

thiol, *N,N'*-ethylene thiourea, and 2-mercapto benzothiazole. The most preferred one is thionicotinamide.

Representative examples of organic dyes include but are not limited to

- 5 Bismarck Brown Y, Chicago Sky Blue 6B, and Acid Violet.

The organic additives are constantly consumed due to breakdown and oxidation in the electroplating process. The consumed additives are generally compensated for by a replenishing process to maintain constant bath chemistry.

- 10 Numerous consumption/replenishment cycles may proceed before a complete replacement of the plating bath is necessary. As a result of this process, there is an accumulation of contaminants which can be a critical problem. The contaminants may interfere with the functioning of organic additives and may cause inconsistent plating that is unacceptable to the semiconductor industry.

15

It has been found that removal of organic additives can be accomplished with activated carbon such as type 4040 and DCL activated carbon from Barneby Scientific Corp. The bath can be filtered through an activated carbon bed and returned to the plating bath without the need for dumping and restocking the plating bath. The

- 20 increased number of cycles without having to remake the bath improve effectiveness and economics of the plating process.

This consumption and breakdown of the plating bath additives will result in the need for replenishment of these additives. An accurate determination is needed in situ and feedback provided fairly rapidly to enable efficient use of baths by semiconductor fabs. The criteria for this analysis include the ability to separate bath components, minimum detection limits, measurement time, accuracy and repeatability and the complexity and frequency of calibration and maintenance. Electrochemical analytical techniques such as cyclic voltammetric stripping (CVS), AC-cyclic voltammetry (AC-CV), AC impedance spectroscopy (AC-IS) and pulsed cyclic galvanostatic analysis (PCGA) have been employed. CVS is generally preferred as it provides relatively high measurement accuracy and fast test results while not generating waste. High performance liquid chromatography (HPLC) is also employed

as it offers the advantage of allowing quantitative measurement of contaminants and determination of break-down additives.

The invention further comprises the use of molecules that combine
5 brightener/carrier and carrier/leveler functionalities. The combination of
brightener/carrier is typically a monomeric to polymeric protein chain where the chain
is linked by sulfide and disulfide bridges. The combination of carrier/leveler can help
improve the stability of the leveler while simplifying the bath by reducing the number
of organic additives. Such materials can be poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-
10 (dimethylamino)propyl]urea, quaternited, and poly(melamine-*co*-formaldehyde),
partially methylated.

The carrier of the present invention may be added in an amount ranging from
about 2 to about 1000 parts per million parts water. The leveler may be added in an
15 amount of about 2 parts to about 1000 parts per million parts of water in the
electroplating solution.

The brightener may be added in an amount ranging from about 5 parts to about
100 parts per million parts water. When the combination carrier/brightener is
20 employed, it is added in an amount ranging from about 5 to about 100 parts per
million parts water. The combination carrier/leveler when employed may be added in
an amount ranging from about 2 to about 1000 parts per million.

Other additives that are found in the baths include wetting agents such as
25 carboxylic acids and antioxidants. Carboxylic acids such as citric acid improve
wetting ability of the cathode and provide better adsorption of the organic additives to
the cathode. Typically, these are added in a range of about 2 to about 1000 parts per
million parts water in the bath.

30 Brighteners tend to be oxidized in the vicinity of the anode during and without
plating. Oxidized brighteners lose their functionality and cause an inconsistent
plating rate and poor quality of the as-plated object. The oxidizing agents near the
cathode are typically hydrogen peroxide and oxygen. The present inventors have

discovered that continuously purging the bath solution near the anode side with an inert gas will expel oxygen out of the solution.

The additive packages of the present invention may be added to the aqueous acid copper electroplating bath either individually or as combinations depending upon the type of substrate being plated.

The plating solutions of this invention are used in a conventional manner. They are preferably used at room temperature or higher temperature. During plating, 10 the bath solution is preferably agitated by inert gas, air sparger or by mechanical means. The plating current density can range between 3 mA/cm² and 40 mA/cm² depending on aspect ratio of trenches and vias. The wave form can be direct current (DC), pulse current (PC) or pulse reverse current (PRC).
15 In studies performed using 67 g/l of CuSO₄·5H₂O, 170 g/l of H₂SO₄ and 45 g/l of C1⁺ as the starting bath, good plating results were obtained using a current density of 3.2 mA/cm² and 25.5 mA/cm² with DC, PC or PRC wave form. The following additive combinations produced the best results regarding trench filling.

	<u>Plating Solution</u>	<u>Composition (PPM)</u>
20	1	C1(20) B1(12) L1 (15)
	2	C1(20) B1(12) L2 (25)
	3	C1(20) B1(12) L3 (25)
	4	C1(20) B1(12) L4 (25)

25 C1 is polyethylene glycol
B1 is 3-mercaptop-1-propanesulfonic acid sodium salt
L1 is poly(diallyldimethylammonium chloride)
L2 is diethylenetriamine
30 L3 is (R)-(-)-thiazoline-4-carboxylic acid
L4 is poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethyl amino)propyl]urea, quaternized, 62 wt. % in water.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and 5 this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

CLAIMS

Having thus described the invention, what we claim is:

1. An acid copper electroplating composition comprising an aqueous solution of an acid and a copper salt, the improvement comprising the addition of at least one of a carrier compound; a water-soluble, mercapto-containing organic brightener compound; and a leveler compound which comprises an organic compound containing single and multiply charged centers.
5
2. The composition as claimed in claim 1 wherein said acid is sulfuric acid.
3. The composition as claimed in claim 1 wherein said copper salt is selected from the group consisting of copper sulfate, copper acetate, copper fluoborate, cupric nitrate and copper pyrophosphate.
4. The composition as claimed in claim 3 wherein said copper salt is copper sulfate.
5. The composition as claimed in claim 1 wherein said carrier compound is selected from the group consisting of a polysaccharide compound, polyethylene glycol and poly(ethylene oxide).
6. The composition as claimed in claim 1 wherein said polysaccharide carrier is selected from the group consisting of starch, cellulose, amylopectin and amylose.
7. The composition as claimed in claim 1 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of *N*-methylallyl-1-*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate;
5 3-mercaptopropanesulfonic acid sodium salt; 3-mercaptopropanesulfonic acid; bis (2-mercaptopethyl) sulfide; ethylene trithio carbonate; ethanethiol; 2-

mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiодиethanol.

8. The composition as claimed in claim 7 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of ammonium diethyldithiocarbamate, 3-mercapto-1-propanesulfonic acid sodium salt, and 3-mercapto-1-propanesulfonic acid.

9. The composition as claimed in claim 1 wherein said leveler is selected from the group consisting of polymeric levelers, low molecular weight levelers and organic dyes.

10. The composition as claimed in claim 9 wherein said polymeric leveler is selected from the group consisting of polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-

5 (dimethylamino)propyl]urea, quaternized; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).

11. The composition as claimed in claim 10 wherein said polymeric leveler is selected from the group consisting of poly[(bis(2-chloroethyl)ether-*alt*-1,2-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(diallyl dimethylammonium chloride).

12. The composition as claimed in claim 9 wherein said low molecular weight leveler is selected from the group consisting of N-containing acyclic compounds, N-containing five-membered heterocyclic compounds and N-containing six-membered heterocyclic compounds.

13. The composition as claimed in claim 12 wherein said low molecular weight leveler is selected from the group consisting of 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, diethylenetriamine, *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride, 5-phenyl-1 *H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1 *H*-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4 *H*-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulfate, 10 hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopyrimidine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercaptop-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinolinethiol, 5-carbethoxy-2-thiouracil, 1 *H*-1,2,4-triazole-3-thiol, 15 1-phenyl-1 *H*-1,2,4-triazole-5-thiol, *N,N'*-ethylene thiourea, and 2-mercaptopbenzothiazole.

14. The composition as claimed in claim 13 wherein said low molecular weight leveler is selected from the group consisting of diethylenetriamine and thionicotinamide.

15. The composition as claimed in claim 9 wherein said organic dye leveler is selected from the group consisting of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

16. The composition as claimed in claim 1 further comprising a brightener/carrier molecule.

17. The composition as claimed in claim 16 wherein said brightener/carrier molecule is polymeric protein.

18. The composition as claimed in claim 1 further comprising a carrier/leveler molecule.

19. The composition as claimed in claim 18 wherein said carrier/leveler molecule is selected from the group consisting of poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl] urea, quaternized, and poly(melamine-co-formaldehyde).

20. The composition as claimed in claim 1 wherein the weight ratio of carrier to leveler to brightener ranges from about 0.09 to 47.6 : 0.09 to 47.6 : 0.2 to 4.7 weight/weight percent.

21. An improved method for making an acid copper electroplating bath comprising an aqueous solution of acid and copper salt, the improvement comprising adding to said bath a carrier compound; a water-soluble, mercapto-containing organic brightener compound; and a leveler compound which comprises an organic compound containing single and multiply charged centers.

22. The method as claimed in claim 21 wherein said carrier compound is selected from the group consisting of a polysaccharide compound, polyethylene glycol and poly(ethylene oxide).

23. The method as claimed in claim 21 wherein said polysaccharide carrier is selected from the group consisting of starch, cellulose, amylopectin and amylose.

24. The method as claimed in claim 21 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of *N*-methylallyl-*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 5 3-mercaptopropanesulfonic acid sodium salt; 3-mercaptopropanesulfonic acid; bis (2-mercaptopropanesulfonic acid) sulfide; ethylene trithio carbonate; ethanethiol; 2-mercaptopropanesulfonic acid; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiobutanethiol.

25. The method as claimed in claim 24 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of ammonium diethyldithiocarbamate, 3-mercapto-1-propanesulfonic acid sodium salt, and 3-mercapto-1- propanesulfonic acid.

26. The method as claimed in claim 21 wherein said leveler is selected from the group consisting of polymeric levelers, low molecular weight levelers and organic dyes.

27. The method as claimed in claim 26 wherein said polymeric leveler is selected from the group consisting of polyethylenimine, 80% ethoxylated; poly (allylamine); poly (allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis (2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, 5 quaternited; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).

28. The method as claimed in claim 26 wherein said polymeric leveler is selected from the group consisting of poly[bis (2-chloroethyl)ether-*alt*-1,3-bis [3-(dimethylamino)propyl]urea, quaternited, and poly (diallyldimethylammonium chloride).

29. The method as claimed in claim 26 wherein said low molecular weight leveler is selected from the group consisting of N-containing acyclic compounds, N-containing five-membered heterocyclic compounds and N-containing six-membered heterocyclic compounds.

30. The method as claimed in claim 26 wherein said low molecular weight leveler is selected from the group consisting of 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, and diethylenetriamine, *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, 5 thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide,

thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride, 5-phenyl-1*H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1*H*-1,2,4-triazole-3-thiol, 2-amino-6 purinethiol, 4-amino-5-(4'-pyridyl)-4*H*-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulfate, hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6 mercaptopyrimidine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercaptop-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithiocyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinolinethiol, 5-carbethoxy-2-thiouracil, 1*H*-1,2,4-triazole-3-thiol, 1-phenyl-1*H*-1,2,4-triazole-5-thiol, *N,N'*-ethylene thiourea, and 2-mercaptop benzothiazole.

31. The method as claimed in claim 30 wherein said low molecular weight leveler is selected from the group consisting of diethylenetriamine and thionicotinamide.

32. The method as claimed in claim 26 wherein said organic dye leveler is selected from the group consisting of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

33. The method as claimed in claim 21 further comprising a brightener/carrier molecule.

34. The method as claimed in claim 33 wherein said brightener/carrier molecule is polymeric protein.

35. The method as claimed in claim 21 further comprising a carrier/leveler molecule.

36. The method as claimed in claim 35 wherein said carrier/leveler molecule is selected from the group consisting of poly[bis(2-chloroethyl/ether-alt-1,3-bis[3-(dimethylamino)propyl]urea, quaternited, and poly(melamine-co-formaldehyde).

37. The method as claimed in claim 21 further adding at least one of an alkaline source compound and a chloride ion-containing compound.

38. The method as claimed in claim 21 wherein said carrier is present in a range of about 2 to 1000 parts per million, said leveler is present in a range of about 2 to 1000 parts per million and said brightener is present in a range of about 5 to 100 parts per million.

39. A method for copper plating of advanced interconnects comprising immersing said interconnects in a copper plating bath comprising an aqueous solution of an acid and a copper salt and at least one of a carrier compound; a water-soluble, mercapto-containing organic brightener compound; and a leveler compound containing single and multiply charged centers.

5 40. The method as claimed in claim 39 wherein said acid is sulfuric acid.

41. The method as claimed in claim 39 wherein said copper salt is selected from the group consisting of copper sulfate, copper acetate, copper fluoborate, cupric nitrate and copper pyrophosphate.

42. The method as claimed in claim 41 wherein said copper salt is copper sulfate.

43. The method as claimed in claim 39 wherein said carrier compound is selected from the group consisting of a polysaccharide compound, polyethylene glycol and poly(ethylene oxide).

44. The method as claimed in claim 43 wherein said polysaccharide carrier compound is selected from the group consisting of starch, cellulose, amylopectin and amylose.

45. The method as claimed in claim 39 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of *N*-methylallyl-

N'-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 3-mercaptopropanesulfonic acid sodium salt; 3-mercaptopropanesulfonic acid; bis(2-mercaptoproethyl) sulfide; ethylene trithio carbonate; ethanethiol; 2-
5 mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiidiethanol.

46. The method as claimed in claim 45 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of ammonium diethyldithiocarbamate, 3-mercaptopropanesulfonic acid sodium salt, and 3-mercaptopropanesulfonic acid.

47. The method as claimed in claim 39 wherein said leveler is selected from the group consisting of polymeric levelers, low molecular weight levelers and organic dyes.

48. The method as claimed in claim 47 wherein said polymeric leveler is selected from the group consisting of polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, 5 quaternized; poly[*N,N'*-bis(2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).

49. The method as claimed in claim 47 wherein said polymeric leveler is selected from the group consisting of poly[(bis(2-chloroethyl)ether-*alt*-1,2-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(diallyl dimethylammonium chloride).

50. The method as claimed in claim 47 wherein said low molecular weight leveler is selected from the group consisting of N-containing acyclic compounds, N-

containing five-membered heterocyclic compounds and N-containing six-membered heterocyclic compounds.

51. The method as claimed in claim 50 wherein said low molecular weight leveler is selected from the group consisting of 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, diethylenetriamine, *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride, 5-phenyl-1*H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1*H*-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4*H*-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulfate, 10 hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopyrimidine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercaptop-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinolinethiol, 5-carbethoxy-2-thiouracil, 1*H*-1,2,4-triazole-3-thiol, 1-phenyl-1*H*-1,2,4-triazole-5-thiol, *N,N*'-ethylene thiourea, and 2-mercaptopbenzothiazole.

15

52. The method as claimed in claim 51 wherein said low molecular weight leveler is selected from the group consisting of diethylenetriamine and thionicotinamide.

53. The method as claimed in claim 47 wherein said organic dye leveler is selected from the group consisting of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

54. The method as claimed in claim 39 further comprising a brightener/carrier molecule.

55. The method as claimed in claim 54 wherein said brightener/carrier molecule is polymeric protein.

56. The method as claimed in claim 39 further comprising a carrier/leveler molecule.

57. The method as claimed in claim 56 wherein said carrier/leveler molecule is selected from the group consisting of poly[bis(2-chloroethyl)ether-alt-1,3-bis-(dimethylamino)propyl] urea, quaternized, and poly(melamine-co-formaldehyde).

58. The method as claimed in claim 39 wherein said carrier is present in the composition in an amount ranging from about 2 to about 1000 parts per million parts water.

59. The method as claimed in claim 39 wherein said leveler is present in the composition in an amount ranging from about 2 to about 1000 parts per million parts water.

60. The method as claimed in claim 39 wherein said brightener is present in the composition in an amount ranging from about 5 to about 100 parts per million parts water.

61. The method as claimed in claim 39 wherein said carrier/brightener is present in an amount ranging from about 5 to about 1000 parts per million parts water and said carrier/leveler is present in an amount ranging from about 2 to about 1000 parts per million parts water.

62. The method as claimed in claim 39 wherein said compounds are added either individually or as combinations to said aqueous solution.

63. The method as claimed in claim 39 wherein a current between 3 mA/cm² and 40 mA/cm² is applied to said solution.

64. The method as claimed in claim 63 wherein the wave form of said current is selected from the group consisting of direct current, pulse current and pulse reverse current.

ABSTRACT

Improved acid copper electroplating bath compositions are disclosed. The improved bath solutions contain at least one of a carrier; a water-soluble, mercapto-containing organic brightener; and a leveler which comprises an organic compound containing single or multiply charged centers in acidic bath solution. These 5 electroplating bath compositions are used to copper plate advanced interconnects on semiconductor devices.

PRINTED IN U.S.A.